The reaction mixture was chilled to −40° and the crystalline product was recovered by filtration. The crystals were washed with cold pentane and dried under vacuum, mp −4 to −6°. Recovery (76 g) amounted to 89% of the ether formed; purity, determined by ultraviolet spectroscopy, was 95%.

Acknowledgment.—The authors gratefully acknowledge the significant contributions to this work made by others at the Hercules Research Center, particularly Evelyn Cook, D. L. Kouba, H. H. Espy, F. E. Williams, J. C. Snyder, F. S. Stow, and F. F. Nelson.

p-Nitrosophenol Chemistry. II. Amination of *p*-Nitrosophenol Ethers with Primary Aromatic Amines

J. T. HAYS, H. L. YOUNG, AND H. H. ESPY

Hercules Research Center, Wilmington, Delaware

Received June 14, 1966

The reaction of alkyl ethers of *p*-nitrosophenol with primary aromatic amines gives *p*-nitrosodiphenylamines in high yields under mild conditions. This reaction is an example of an acid-catalyzed aromatic nucleophilic displacement in which the protonated nitroso group exerts a strong activating effect. Reduction or reductive alkylation of the *p*-nitrosodiphenylamine product provides a simple and unique route to *p*-aminodiphenylamine and its derivatives, currently of commercial importance as antiozonants for rubber.

As indicated in the first paper in this series,[1] the phenolic hydroxyl group of *p*-nitrosophenol can be replaced by an amino group through reaction of its ethers with primary amines. The drastic conditions generally required for direct replacement of a phenolic hydroxyl with an amino group have previously made this type of reaction of little importance in the benzene series.[2] Certain activated phenols (and their ethers) such as those with *o*- and *p*-nitro groups do undergo such replacement reactions.[3,4] Likewise the hydroxyl group of *p*-nitrosophenol has been replaced by fusion with ammonium salts.[5,6] However, according to literature reports, reaction of *p*-nitrosophenol with aniline gives *p*-hydroxyazobenzene in the presence of acetic acid,[7] azophenine on heating with the hydrochloride,[8] or an indoaniline with strong sulfuric acid.[9] These reactions are all avoided and *p*-nitrosodiphenylamines are obtained in high yields under mild conditions when the ethers of *p*-nitrosophenol, presumably in a strongly activated protonated form,[1] react with primary aromatic amines.

$$p\text{-NOC}_6\text{H}_4\text{OR} + \text{H}_2\text{NC}_6\text{H}_4\text{R}' \xrightarrow{\text{H}^+} p\text{-NOC}_6\text{H}_4\text{NHC}_6\text{H}_4\text{R}' + \text{ROH}$$

This reaction is an interesting example of an acid-catalyzed aromatic nucleophilic substitution. Reduction or reductive alkylation of the *p*-nitrosodiphenylamine product provides a simple and unique route to *p*-aminodiphenylamine and its derivatives, currently of commercial importance as antiozonants for rubber.[10]

Our initial attempts to carry out the replacement of the phenolic hydroxyl by direct reaction of *p*-nitrosophenol with amines gave negative results except in alcohol solutions with acid catalysts. Aniline and *p*-nitrosophenol were found to react at room temperature under these conditions to form *p*-nitrosodiphenylamine. Low and variable yields were related to time of contact between *p*-nitrosophenol and acidic alcohol solutions and were then shown to depend on the equilibrium set up between *p*-nitrosophenol and its ethers.[1]

The ether was shown to be the reactive species under these conditions by adding aniline to acidified ethanolic solutions of *p*-nitrosophenol at various times and concentrations. Maximum yields of *p*-nitrosodiphenylamine corresponded to equilibrium concentrations of the ether. Isolation of the pure ether and reaction with aniline gave high yields and conversions to *p*-nitrosodiphenylamine.

Scope of the Amination Reaction.—The replacement of the alkoxy group of a *p*-nitrosophenyl alkyl ether with an amino group has been extended to a variety of ethers of *p*-nitrosophenol and a number of primary aromatic amines. Ultraviolet analysis of reaction mixtures has shown that high conversions (90–95%) to *p*-nitrosodiphenylamine have been obtained by the reaction of aniline with the methyl, ethyl, and 1-butyl ethers (Table I). *p*-Nitrosodiphenylamine has been isolated in conversions of 80–85%. In addition, formation of *p*-nitrosodiphenylamine was qualitatively demonstrated by means of ultraviolet spectra for the reaction of aniline with *p*-nitrosophenol ethers from the following alcohols: 2-octyl, cyclohexyl, 2-ethoxyethyl, oleyl, isoamyl, benzyl, allyl, and cetyl.

Yields and properties of the products of the reaction of the ethyl ether (*p*-nitrosophenetole) with a number of monosubstituted anilines are shown in Table II. Amines with electron-donating substituents gave good yields. Although the products from amines with electron-withdrawing substituents were qualitatively identified, the yields were poor and the products were not completely characterized.

In the absence of acid, little or no reaction takes place. In the presence of acid, the reaction is quite rapid at low temperatures (25–50°). For optimum results an aniline to acid mole ratio of about 10–20:1 is required. The reaction rate increases with acid concentration; however, high acid concentration leads

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(1) Preceding paper: J. T. Hays, E. H. deButts, and H. L. Young, *J. Org. Chem.*, **32**, 153 (1967).

(2) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," revised and rewritten by T. W. J. Taylor and W. Baker, Oxford University Press, New York, N. Y., p 48.

(3) K. Jedlicke, *J. Prakt. Chem.*, **48** (1893).

(4) R. L. Burwell, *Chem. Rev.*, **54**, 615, 665 (1954).

(5) O. Fischer and E. Hepp, *Ber.*, **20**, 2477 (1887); O. Fischer and E. Schaffer, *Ann.*, **286**, 151 (1895).

(6) J. Willenz, *J. Chem. Soc.*, 2049 (1955).

(7) C. Kimich, *Ber.*, **8**, 1027 (1875).

(8) O. N. Witt and E. G. P. Thomas, *J. Chem. Soc.*, **43**, 115 (1883).

(9) E. H. Rodd, "Chemistry of Carbon Compounds," IIIB, Elsevier Publishing Co., New York, N. Y., 1956, p 721.

(10) B. S. Biggs, *Rubber Chem. Tech.*, **31**, 1015 (1958).

TABLE I

p-NITROSODIPHENYLAMINE FROM ANILINE AND ALKYL ETHERS OF p-NITROSOPHENOL

Ether	Acid	Solvent	Concn, moles/l. Aniline	Acid	Ether	Reacn temp, °C	Reacn time, hr	Conversion to p-nitrosodiphenylamine,[a] %
Methyl	HCl	Methanol	2.2	0.2	2.0	30	0.2	75
							1.1	96
Ethyl	HCl	Ethanol	0.85	0.07	0.85	25	4.4	86
							21	97
1-Butyl	p-TSA[b]	1-Butanol	2.2	0.2	2.0	25	2.0	90
							4.0	93
			2.2	0.2	2.0	35	2.0	91–94
							4.0	90
			2.0	0.2	2.0	35	2.0	77
							3.0	84
1-Butyl	HCl	1-Butanol	3.0	0.3	2.0	35	0.5	95
							2.0	95
1-Butyl	p-TSA[b]	1-Butanol (3% water)	2.2	0.2	2.0	35	2.0	88
							4.0	91
1-Butyl	H_2SO_4	1-Butanol	2.2	0.1	2.0	35	2.5	28
1-Butyl	p-TSA[b]	1-Butanol	2.2	0.2	2.0	50	0.75	86
							1.0	84
							2.0	79
1-Butyl	Acetic	1-Butanol	2.2	0.2	2.0	35	3.0	8
			2.2	1.1	2.0	35	3.0	59
			2.2	2.2	2.0	35	3.0	79
			2.2	3.3	2.0	35	3.0	82
1-Butyl		Acetic Acid	2.2		2.0	35	3.0	76
1-Butyl	p-TSA[b]	Aniline		0.15	1.5	35	2.0	83
							4.0	80

[a] Conversions based on analysis of reaction mixtures using ultraviolet absorption spectroscopy. [b] p-Toluenesulfonic acid monohydrate.

to lower conversions owing to decomposition reactions of the p-nitrosodiphenylamine. Hydrogen chloride or p-toluenesulfonic acid monohydrate was used as the catalyst in most of our work. Sulfuric acid was less satisfactory since aniline sulfate is essentially insoluble in the reaction mixture. Acetic acid gave reasonable rates of reaction only when present in large amounts (Table I).

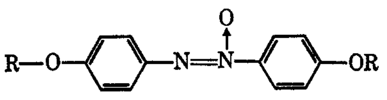
In most of our work, the alcohol corresponding to the ether was used as the solvent. Small amounts (up to 3%) of water in the alcoholic solvents have no appreciable effect on the reaction. Therefore, concentrated hydrochloric acid can be added to the reaction mixture as the catalyst. No study was made on the effect of large amounts of water, since water in the presence of acid will hydrolyze the p-nitrosophenyl alkyl ethers back to the phenol. Consequently, the reactants should be mixed so that the ether is not contacted with acid in the absence of the amine. In the presence of the basic amine, no appreciable hydrolysis will occur.

Both glacial acetic acid (without added catalyst) and excess aniline were used as solvents, but the conversions to p-nitrosodiphenylamine were somewhat lower (75–85% *vs.* 90–95%) than those obtained in alcohols under the same conditions (Table I).

The amination reaction can be carried out over a broad temperature range; however, it is most conveniently run at 25–50°. Higher temperatures increase by-product formation and reduce the maximum conversion to p-nitrosodiphenylamine.

Closely related to reaction temperature and catalyst concentration is the reaction time. The amination reaction reaches a maximum conversion to p-nitrosodiphenylamine, which then decreases with time as the result of side reactions. This decrease is most evident at higher temperatures (*i.e.*, >50°); however, at 30° or less the reaction products are more stable and decomposition is negligible for periods up to 6 hr. Under the prescribed reaction conditions the reaction time is 2–3 hr.

Under optimum conditions the amination of p-nitrosophenyl ethers with aniline is a clean reaction with less than 4% by-products. The only identified by-products were small amounts of the p,p′-dialkoxyazoxybenzenes, shown below. Only trace amounts of an azo-type compound were observed spectroscopically.



The essentially complete absence of condensation at the nitroso group to form azo compounds must be emphasized. This is most unexpected since this reaction is also acid catalyzed and may be carried out in aqueous alcohol.[11]

Preparative Methods.—Two general synthetic methods are available, starting with the pure p-nitrosophenyl ether or generating the ether *in situ*. In the first case, best results are achieved with an ether concentration of about 2 *M* and a slight excess (5–20%) of aniline. At this level the bulk (~80%) of the product precipitates from the reaction mixture and can be recovered in a purity of about 90% by simply filtering the chilled (0–10°) reaction mixture.

In the second synthetic method, the p-nitrosophenyl ether is not isolated prior to reaction with aniline. p-Nitrosophenol is simply equilibrated with an alcohol.

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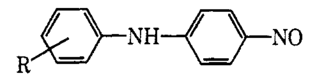
[11] Y. Ogata and Y. Takagi, *J. Am. Chem. Soc.*, **80**, 3591 (1958).

TABLE II

p-NITROSODIPHENYLAMINES FROM *p*-NITROSOPHENETOLE AND AROMATIC AMINES[a]

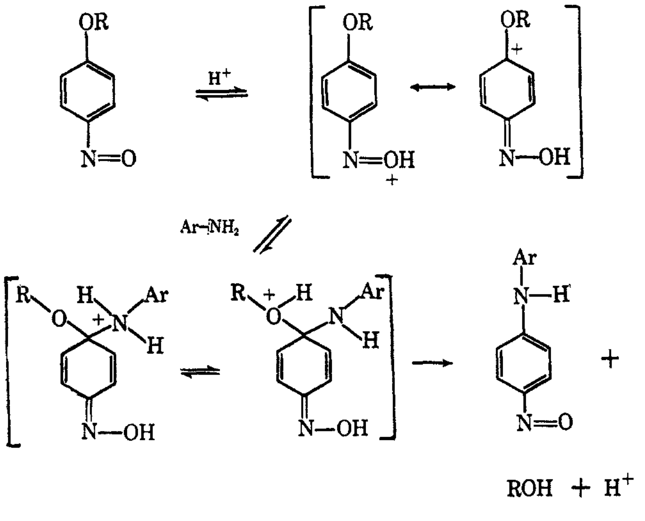


	Ultraviolet spectra					Anal, %			
						Calcd		Found	
Substituent (R)	λ_{max}, mμ	ε × 10^{-3}	Mp, °C	Ref	Conversion,[b] %	C	H	C	H
H	263	10.6	144–145	*c*	74[d]	72.7	5.1	72.5	5.2
	427	29.7							
o-CH_3	265	7.6	148		63	73.5	5.7	73.7	5.7
	418	31.0							
m-CH_3	264	10.2	124		59	73.5	5.7	73.3	5.9
	430	29.3							
p-CH_3	267	9.9	172–173	*e*	85	73.5	5.7	74.1	5.7
	431	30.2							
p-OCH_3	268	8.3	164–166	*f*	92	68.4	5.3	68.2	5.4
	431	24.9							
p-OC_2H_5	268	9.2	158–160	*g*	92	69.4	5.8	69.9	5.9
	431	26.9							
p-Cl	268	10.9	157–160	*h*	84	61.9	3.9	62.0	4.0
	425	29.1							
p-NH_2	267	10.2	168		84[i]	67.5	5.2	67.9	5.3
	437	24.7							
p-$N(CH_3)_2$	266	14.2	175		78[j]	69.7	6.3	69.7	6.1
	440	20.7							
p-(p-NOC_6H_4NH-)	273	>5.1							
	450	>11.0							
p-COOH	270–300	9.6	>360						
	425	28.4							
p-NO_2	233	10.9	185						
	350	Sh[k]							
	427	26.7							
p-CN	270	Sh[k]	196						
	295	11.2							
	419	32.7							

[a] Ethanol solvent, 5 mole % HCl on basis of amine, 24-hr reaction time. [b] Conversions based on initial amount of *p*-nitrosophenetole. [c] O. Fischer and E. Hepp, *Ber.*, **19,** 2991 (1886). [d] 10 mole % HCl. [e] A. Reichold, *Ann.*, **255,** 162 (1889). [f] R. Willstätter and H. Kubli, *Ber.*, **42,** 4135 (1909). [g] P. Jacobson, F. Henrich, and J. Klein, *ibid.*, **26,** 688 (1893). [h] M. Ikuta, *Ann.*, **243,** 272 (1888). [i] 48-hr reaction time. [j] 4.5-hr reaction time. [k] Shoulder.

Aniline and catalyst are then added directly to this reaction mixture. Unreacted *p*-nitrosophenol does not interfere with the amination reaction.

Mechanism.—A reasonable mechanism that may be postulated to explain the acid catalysis involves reaction between the amine nucleophile and a protonated form of the *p*-nitrosophenyl ether. Although the proton will be distributed among the various basic species present in the system, it will exist predominantly on the amine. The suggested mechanism assumes that the acid concentrations used in these reactions are sufficient to provide a kinetically significant concentration of the protonated ether.



This amination reaction is an example of an acid-catalyzed aromatic nucleophilic displacement reaction in which the protonated nitroso group exerts a strong activating effect at the *para* position. Analogous acid-catalyzed amination reactions have been reported for the displacement of halogens and alkoxy groups in heterocyclic systems in which a protonated heteronitrogen is the activating group.[12] Similar acid-catalyzed hydrolysis reactions in the pyridine system are also known.[13] Another activating group for acid-catalyzed aromatic nucleophilic displacement reactions is the protonated azo linkage, which facilitates the hydrolysis of phenylazo-1-naphthyl ethers and the etherification of the corresponding naphthols.[14] The conversion of enols (dimethyldihydroresorcinol and *β*-naphthol) to ethers by the acid-catalyzed reaction with alcohols also belongs in this category.[15] The latter two reactions are directly analogous to the formation and hydrolysis of *p*-nitrosophenyl ethers reported previously.[1]

(12) J. F. Bunnett and R. Zahler, *Chem. Rev.*, **49,** 331 (1951).

(13) J. D. Reinheimer, J. T. Gerig, R. Garst, and B. Schrier, *J. Am. Chem. Soc.*, **84,** 2770 (1962).

(14) J. F. Bunnett, E. Buncel, and V. K. Nahabedian, *ibid.*, **84,** 4136 (1962).

(15) K. B. Wiberg and K. A. Saegebarth, *J. Org. Chem.*, **25,** 832 (1960).

All of these reactions may be considered to proceed by the same basic mechanism, involving the activation of an aromatic carbon atom to nucleophilic attack by protonation of a functional group conjugated with the aromatic system. As noted by Bunnett,[14] protonation provides the substrate with the capacity to accept the pair of electrons from the nucleophile during the bimolecular substitution at the activated carbon atom.

Experimental Section

***p*-Nitrosophenyl Ethers.**—The methyl, ethyl, and 1-butyl ethers of *p*-nitrosophenol used in this work were prepared from acidified solutions of *p*-nitrosophenol in the appropriate alcohol as described previously.[1]

Analytical Methods.—Ultraviolet spectra were recorded by a Cary Model 11 recording spectrophotometer operated at a scanning speed of 4 mμ/sec, with the slit width set at 0.1 mm at 270 mμ. Silica cells (1 cm) were used. The ultraviolet absorption spectra of the *p*-nitrosophenyl ethers in isooctane were reported previously.[1] The absorption maxima and molar absorptivities of the methyl, ethyl, and 1-butyl ethers in ethanol are summarized in Table III. The starting *p*-nitrosophenyl ethers used in this work were assayed using these absorptivities. Stock solutions, usually 4 *M*, were diluted 1:50,000 with 3A ethanol[16] and the ether purities were estimated from the absorbance of the 340–345-mμ maximum.

TABLE III

ULTRAVIOLET ABSORPTION BANDS OF *p*-NITROSOPHENYL ALKYL ETHERS IN ETHANOL

Ether	λ_{max}, mμ	Molar absorptivity, $\epsilon \times 10^{-3}$
Methyl	342	17
	242	
Ethyl	344	18.6
	242	7.55
1-Butyl	345	17.9
	241	7.34

The ultraviolet spectrum of *p*-nitrosodiphenylamine shows a major absorption maximum at 427 and a minor maximum at 262 mμ in neutral to slightly acidic (acetic acid) ethanol. Strong inorganic acids cause decomposition of *p*-nitrosodiphenylamine. In ethanolic KOH (0.01 *M*), a major absorption maximum occurs at 382 and two minor maxima occur at 295 and 253 mμ. Solvent shifts also occur. The absorption maxima and molar absorptivities of *p*-nitrosodiphenylamine are summarized in Table IV. The maxima observed under both acidic and basic conditions are similar to those in the literature.[17] The spectra of the substituted *p*-nitrosodiphenylamines are similar to that of the parent compound and are summarized in Table II. The purity of crude *p*-nitrosodiphenylamine products was estimated from the absorbance at 427 mμ in *ca.* 10^{-5} *M* acidic ethanol solutions, assuming ε 29,700 for pure material.

The amination reaction was readily followed spectroscopically by simple diluting samples 1:50,000 or 1:62,500 with ethanol containing *ca.* 0.1% acetic acid and recording the spectra (300–500 mμ). Two distinct absorption maxima were obtained, at 427 and at 340–345 mμ. Under such slightly acid conditions, none of the components of the reaction mixture interfere with the absorption maximum of *p*-nitrosodiphenylamine at 427 mμ. The unreacted *p*-nitrosophenyl ethers were determined by their maxima at 340–345 mμ, corrected for minor absorption at this wavelength due to the product, *p*-nitrosodiphenylamine (see Table IV).

p-Nitrosophenol formed by side reactions was assayed spectroscopically, after dilution of the mixture with 0.1% ethanolic KOH, from the maximum of the nitrosophenoxide anion at 405 mμ (ε 32,000). Under these conditions, the maximum of nitrosodiphenylamine was shifted to 382 mμ and was less well resolved from the nitrosophenyl ether peak at 340–345 mμ.

TABLE IV

ABSORPTION BANDS OF *p*-NITROSODIPHENYLAMINE

Medium	λ_{max}, mμ	Molecular absorptivity, $\epsilon \times 10^{-3}$
95% ethanol, acidic[a]	427	29.7
	343[b]	1.39
	262	9.90
95% ethanol, basic[c]	382	28.7
	295	4.36
	253	4.95
Methylene chloride	408	26.7
	261	8.91
Isooctane	385	26.7
	258	9.90

[a] Acetic acid used; strong inorganic acids cause decomposition reactions. Neutral solutions have the same absorption maximum and molar absorptivity. [b] *p*-Nitrosodiphenylamine does not have an absorption maximum at this wavelength; this absorptivity was used in the estimation of the *p*-nitrosophenyl ethers to correct the absorption at 343 mμ due to the product *p*-nitrosodiphenylamine. [c] Ethanolic KOH (0.01 *M*).

Dumas nitrogen analyses were generally 1–2% lower than the calculated amounts, despite satisfactory carbon, hydrogen, and frequently, oxygen analyses.

Reaction of Aniline with *p*-Nitrosophenol.—Solutions of aniline (0.2 *M*), *p*-nitrosophenol (0.2 *M*), and hydrogen chloride (0.1 *M*) in dimethylformamide, dimethyl sulfoxide, and glacial acetic acid were stirred at 25° for 50 hr. A similar solution in acetic acid, but with no hydrogen chloride, was stirred at 25° for 2 hr and at 75° for 1 hr. Also, a solution in tributyl phosphate, 1 *M* in aniline, and *p*-nitrosophenol, 0.5 *M* in hydrogen chloride, was stirred at 25° for 7 hr. Samples (1.0 ml) of the reaction mixtures were analyzed by ultraviolet spectroscopy; apparent conversions to *p*-nitrosodiphenylamine ranged from 2 to 5%.

Reaction of Aniline with *p*-Nitrosophenol Alkyl Ethers Generated *in situ*.—Into a 2-l. flask equipped with a mechanical stirrer, dropping funnel, and thermometer was charged 15.2 g (80 mmoles) of *p*-toluenesulfonic acid monohydrate, 410 ml of methanol, and 73.8 g (558 mmoles) of dry 93% pure *p*-nitrosophenol. The solution was stirred for 1 hr at 20–25°.

Aniline (48.9 g, 526 mmoles) was then added to the above equilibrium mixture and stirred for 3.5 hr at 27–34°. During this time a large amount of blue *p*-nitrosodiphenylamine crystals precipitated. At this point, 29.4 g (350 mmoles) of sodium bicarbonate in 400 ml of water was added to neutralize unreacted *p*-nitrosophenol and the acid catalyst. During the addition, the reaction mixture was cooled to 24° with a water bath and held for another 30 min at this temperature to allow all the *p*-nitrosodiphenylamine to precipitate. The mixture was filtered and the solid product was washed with four 100-ml portions of water and dried to constant weight at room temperature in a vacuum desiccator, yielding 74.1 g. Ultraviolet absorption analyses of the solid product and the filtrate gave the following values: purity of *p*-nitrosodiphenylamine, 96%; unreacted *p*-nitrosophenol in the filtrate, 35% of the original; material balance for *p*-nitrosophenol, 100%; material balance for aniline, 97%.

The 2-octyl, cyclohexyl, 2-ethoxyethyl, oleyl, isoamyl, benzyl, allyl, and cetyl ethers of *p*-nitrosophenol were also treated with aniline in a similar manner. *p*-Nitrosophenol (20 mmoles) was equilibrated with the corresponding alcohol (40–260 mmoles) for 2 hr at 25° using *p*-toluenesulfonic acid (3.2 mmoles) as catalyst.[1] An equimolar amount of aniline was added and the resulting reaction mixtures were stirred at room temperature for 24 hr. Analysis by ultraviolet spectroscopy showed an absorption band with a maximum at 427 mμ.

Reaction of Aniline with *p*-Nitrosophenyl Alkyl Ethers.—The following general procedure was followed to obtain the data in Table I. Stock solutions of the *p*-nitrosophenyl alkyl ether and of aniline plus the acid catalyst in the desired alcohol solvent were prepared. The appropriate amount of ether was charged to a volumetric flask (10 or 25 ml), dissolved in the alcohol, and brought to volume at room temperature. The ether stock solutions were a bright green in color and were assayed by their ultraviolet spectra prior to use. Similarly, the appropriate amounts of aniline and acid were charged to a volumetric flask,

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[16] 5% methanol, 95% ethanol.

[17] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, *Anal. Chem.*, **23**, 1743 (1951).

dissolved, and brought to volume. *p*-Toluenesulfonic acid was added as the monohydrate. Hydrogen chloride was added in three forms, as aniline hydrochloride, as an alcoholic solution, or as concentrated (37%) hydrochloric acid. When sulfuric acid was employed as catalyst, it was weighed and charged to the reaction flask separately.

The reactions were initiated by adding 2.0 ml of the ether solution (usually 4.0 *M*) to 2.0 ml of the aniline (4.4 *M*)-acid (0.4 *M*) solution in a 30-ml graduated test tube. The solutions were well mixed, and the total volume was determined. The dark brown to red-brown reaction mixtures were stirred magnetically, under a nitrogen atmosphere in a constant-temperature bath (±1°). After an appropriate period, the entire reaction mixture was initially diluted (1:62.5) to 250 ml with 3A ethanol, then further diluted to 1:62,500 with 3A alcohol. The ultraviolet–visible absorption spectra (3000–5000 A) were obtained and the conversion to *p*-nitrosodiphenylamine was estimated as described above.

Reactions in glacial acetic acid and excess aniline were carried out in an analogous manner. Separate solutions in acetic acid of aniline and of the 1-butyl ether of *p*-nitrosophenol were prepared in volumetric flasks (10 ml). Reaction was initiated by mixing equal volumes (2.0 ml); no additional acid catalyst was employed. Reactions in excess aniline were carried out by preparing and mixing solutions of *p*-toluenesulfonic acid and the 1-butyl ether of *p*-nitrosophenol in aniline. Reaction mixtures with both solvents were analyzed spectroscopically.

Reaction of Aniline with *p*-Nitrosoanisole.—A solution (10 ml) of 4.0 *M* *p*-nitrosoanisole (0.040 mole) in a methanol (40 vol. %)-toluene (60 vol. %) mixture was added to 10 ml of a 4.0 *M* (0.040 mole) aniline–0.2 *M* (0.002 mole) *p*-toluenesulfonic acid monohydrate solution in absolute methanol contained in a 125-ml centrifuge tube. The tube was capped, flushed with nitrogen, and placed in a bath at 50°. The reaction mixture was stirred magnetically for 90 min at 50°, then chilled in a ice bath, and centrifuged. The mother liquor was decanted and the dark blue solid was washed with two 20-ml portions of pentane. The solid was dried at 60° under reduced pressure for 6.5 hr: weight 7.1 g, mp 134–139°. Assay by its ultraviolet spectrum showed the material to be 90% by weight *p*-nitrosodiphenylamine; conversion was 81%.

Reaction of Aniline with *p*-Nitrosophenetole.—*p*-Nitrosophenetole (50.2 g, 0.33 mole) was charged to a 1-l., three-necked flask and dissolved in 175 ml of absolute ethanol. The reaction flask, equipped with a mechanical stirrer and an inlet for nitrogen, was flushed with nitrogen; an atmosphere of nitrogen was thereafter maintained over the reaction mixture throughout the reaction period. A slurry of 30.9 g (0.33 mole) of aniline and 1.51 g (0.015 mole) of concentrated H_2SO_4 in 140 ml of absolute ethanol was added with stirring. The aniline sulfate is only slightly soluble in ethanol at room temperature. The reaction mixture was stirred at room temperature for 16.5 hr, neutralized with 22 ml of 10% alcoholic KOH, and filtered by suction. A dark blue solid was separated, washed with three 50-ml portions of pentane, and air dried: weight 45.7 g, mp 139.5–144°.

The filtrate and washings were combined, filtered to remove a small amount of K_2SO_4, and evaporated on the steam bath. The dark red-brown, viscous residue was taken up in 50 ml of methanol and allowed to crystallize at about −30°. A dark blue-black solid was collected by filtration, washed with three 50-ml portions of pentane, and air dried: weight 7.9 g, mp 133–137°. Total crude product was 53.6 g, conversion being 81.5%.

The combined crops of crude products were crystallized from methanol to give 42.0 g of purified *p*-nitrosodiphenylamine, mp 144–145°. The product was identified by its melting point, mixture melting point, and superposition of infrared spectrum with that of an authentic sample (Eastman White Label).

Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; O, 8.08. Found: C, 72.36, 72.56; H, 5.19, 5.24; O, 8.35.

Reaction of Aniline with *p*-Nitrosophenyl 1-Butyl Ether. A.—A solution (10 ml) of aniline (4.0 *M*, 0.040 mole) and aniline hydrochloride (0.4 *M*, 0.004 mole) in 1-butanol was added to 10 ml of a 4.0 *M* (0.040 mole) *p*-nitrosophenyl 1-butyl ether solution in 1-butanol contained in a 125-ml centrifuge tube. The tube was capped, flushed with nitrogen, and placed in a bath at 35°. After being stirred for 2.5 hr at 35°, the reaction mixture was chilled in an ice bath and centrifuged, and the precipitate was washed with three 25-ml portions of pentane. The dark blue-black solid was dried at 55°: weight 7.03 g, mp 126–133°. Assay by its ultraviolet spectrum showed the material to be 95% by weight *p*-nitrosodiphenylamine; conversion was 85%.

B.—A reaction mixture from the preparation of *p*-nitrosophenyl 1-butyl ether by the reaction of *p*-nitrosophenol with acidified 1-butanol with removal of water formed as described previously[1] had the following composition, which was determined spectrophotometrically: 0.463 mole *p*-nitrosophenyl 1-butyl ether, 0.024 mole *p*-nitrosophenol, 0.0126 mole sulfuric acid. The solvent was 1-butanol and the volume was 157 ml.

This mixture was transferred to a 500-ml, three-necked flask equipped with a mechanical stirrer, thermometer, and inlet tube for nitrogen. The flask was flushed with nitrogen and immersed in a bath at 35°. To this mixture was added a slurry of 53.2 g (0.572 mole) of aniline and 4.6 ml (0.057 mole) of 38% hydrochloric acid. The reaction mixture was stirred at 35° for 2 hr and then treated with 137 ml of 2.5% NaOH (0.088 mole) to pH 10. Two phases resulted. The upper 1-butanol layer was separated and treated with 147 ml of 2.5% hydrochloric acid (0.102 mole) to pH 2. The 1-butanol layer was again separated and then filtered. The *p*-nitrosodiphenylamine product was collected, washed with 50 ml of cold 1-butanol, and dried at room temperature under reduced pressure: weight 73.6 g (0.371 mole), mp 143–144°. Purity by ultraviolet assay was 99%, conversion being 80%.

Reaction of Substituted Anilines with *p*-Nitrosophenetole.—The following general procedure was followed to obtain the data in Table II. Solutions 1 *M* in *p*-nitrosophenetole, 1.0–1.1 *M* in the substituted aniline, and 0.025–0.1 *M* in HCl in absolute ethanol and containing 0.04% water were prepared and allowed to stand at 25° for the indicated time. The reaction mixtures were then chilled in an ice bath and filtered. The crude products were recrystallized from methanol or ethanol.

Some crude products, especially those from *p*-phenylenediamine and N,N-dimethyl-*p*-phenylenediamine, were contaminated with a brown, crystalline by-product. This material, the azoxyphenetole, was removed by a benzene wash before recrystallization.

When acetic acid was used as the solvent, no HCl was added. The crude product sometimes crystallized out of the acetic acid solvent, but frequently had to be precipitated by the addition of water.

Acknowledgment.—The authors gratefully acknowledge the significant contributions to this work made by others at the Hercules Research Center, particularly Evelyn Cook, E. H. deButts, D. L. Kouba, W. B. Hewson, L. G. Maury, F. F. Nelson, and F. E. Williams.